THEORETICAL CALCULATION AND VALIDATION
OF THE WATER VAPOR CONTINUUM ABSORPTION

Final Progress Report

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Abstract of the Proposal

The primary objective of this investigation is the development of an improved parameterization of the water vapor continuum absorption through the refinement and validation of our existing theoretical formalism. The chief advantage of our approach is the self-consistent, first principles, basis of the formalism which allows us to predict the frequency, temperature and pressure dependence of the continuum absorption as well as provide insights into the physical mechanisms responsible for the continuum absorption. Moreover, our approach is such that the calculated continuum absorption can be easily incorporated into satellite retrieval algorithms and climate models.

Accurate determination of the water vapor continuum is essential for the next generation of retrieval algorithms which propose to use the combined constraints of multi-spectral measurements such as those under development for EOS data analysis (e.g., retrieval algorithms based on MODIS and AIRS measurements); current Pathfinder activities which seek to use the combined constraints of infrared and microwave (e.g., HIRS and MSU) measurements to improve temperature and water profile retrievals, and field campaigns which seek to reconcile spectrally-resolved and broad-band measurements such as those obtained as part of FIRE. Current widely used continuum treatments have been shown to produce spectrally dependent errors, with the magnitude of the error dependent on temperature and abundance which produces errors with a seasonal and latitude dependence. Translated into flux, current water vapor continuum parameterizations produce flux errors of order 10 W/m^2, which compared to the 4 W/m^2 magnitude of the greenhouse gas forcing and the 1-2 W/m^2 estimated aerosol forcing is certainly climatologically significant and unacceptably large.

While it is possible to tune the empirical formalisms, the paucity of laboratory measurements, especially at temperatures of interest for atmospheric applications, preclude tuning the empirical continuum models over the full spectral range of interest for remote sensing and climate applications. Thus, we propose to further develop and refine our existing far-wing formalism to provide an improved treatment applicable from the near-infrared through the microwave. Based on the results of this investigation, we will provide to the remote sensing/climate modeling community a practical and accurate tabulation of the continuum absorption covering the near-infrared through the microwave region of the spectrum for the range of temperatures and pressures of interest for atmospheric applications.

Final Progress Report

Before starting the present investigation, we knew that there were uncertainties associated with the various approximations introduced in the theoretical water vapor continuum calculations, but we did not know which of these approximations were the most important in determining the accuracy of the results. During the first-year of the grant, we found out that the cut-off procedure is mainly responsible for the uncertainties, and that a more realistic potential model to represent the molecular interaction is crucial to obtain accurate results. The former approximation in which one had to limit the number of states that can be included arose as a consequence of computer limitations. It was expected that as more and more states were included, the calculated approximate results would converge quickly towards the true results. However, it turns out that the convergence is very slow so that for most systems of interest, one is unable to obtain converged results within reasonable computer resources. Therefore, the goal of achieving converged results became a serious challenge to the success of our method. Fortunately, we have found that by choosing the eigenfunctions of the orientation of the two colliding molecules instead of their internal states as the basis set in Hilbert space, one is able to take into account as many states as desired. In this approach, the main computational task becomes the carrying out of multidimensional integrations over the continuous orientational variables. In practice, these integrals are approximated by multidimensional summations over discrete values, the number of which is determined by the resolution required so that the approximated integrals are close to their exact values. For systems consisting of two linear molecules, by choosing proper resolutions based on the functional behavior of the integrands, one is able to evaluate the required integrals within reasonable CPU time. As reported in our previous progress report and published recently (see Pub. 3) for such systems as CO_2 - CO_2 and CO_2 - N_2, the convergence problem was overcome in the second year of the grant. Accordingly, during the third year of the grant we focused on the remaining problem of introducing a more realistic interaction potential in the framework of the theory. We have recently succeeded and have calculated the far-wing line shape and corresponding absorption coefficient for the ν_3 band of self-broadened CO_2 for a number of temperatures between 218 K and 751 K, and we obtained very good agreement with the existing laboratory data for all the temperatures considered (see Pub. 4). Given the fact that the comparisons are made over a large temperature range and that they are produced using the same potential model, we feel confident that the temperature dependence is correctly included in the theory and that one can extend these results to higher or lower temperatures with comparable accuracy. Recently, we have extended the theory to systems involving symmetric-top and asymmetric-top molecules (e.g., H_2O - H_2O or H_2O - N_2) and have obtained converged results for the far-wing line shapes for these systems. This work is currently being written up for publication and fulfills the primary objective of the proposed research.

We now discuss briefly, the new method for the incorporation of a realistic potential model, despite the fact that the interaction potential between two water molecules or between a water molecule and a different perturber is complicated and a detailed representation is not yet fully realized. In general, the potential consists of two parts: an isotropic part and an anisotropic part, and it is well known that the anisotropic part is mainly responsible for the collisional broadening. In our previous formalism, we were limited in the forms of the anisotropic potential that could be treated to simple models. As a result, these models were not expected to be able

to represent realistically the true interaction, and thus would limit the accuracy of the results. However, we have managed to overcome this last drawback during the third of the grant so that we are now in a position to obtain accurate results using a much more sophisticated interaction potential model. The new method is now briefly summarized.

In our previous method, a set of frequencies was first determined from the range of frequencies of interest in the line shape. The procedure then consists of two steps. First, for each of the frequencies (i.e., the energy of the photon absorbed or omitted during the transition process), one determined all accessible combinations of the initial and final positions of the two molecules such that, after a transition has taken place, the values of the anisotropic interaction differ by just the same amount (conservation of energy). Then one calculates contributions to the line shape from each of these combinations and added them up to obtain the magnitude of the line shape corresponding to this frequency. However, a difficulty arose in determining these positions. Within the quasistatic approximation applicable to the far-wing line shape calculation, the position of the two molecules and also the interaction between them are described by the quantum variables necessary to specify their orientations and one classical parameter representing the distance between their centers of mass. During a transition process, the two molecules change their orientations, but not the distance. As a result, for the specified initial and final quantum variables, conservation of energy in the transition process is expressed by an equation involving the distance. By solving this equation to find its roots, the positions of the system are completely determined. It is well known that to find the roots of an equation is not easy unless the equation is of a certain type; more specifically, a polynomial whose order is quadratic or less. Unfortunately, in general, more realistic forms not of the type above were excluded from consideration, unless one could find a method to overcome this difficulty.

During the course of the third year's research, we have developed an inverse method to obviate this limitation on the form of the anisotropic interaction. Besides first choosing the set of frequencies, we choose a set of distances such that they cover the full range of interactions as well. Then, as the next step, for specified initial and final orientations, we calculate the anisotropic energy differences corresponding to each distance chosen and also compute their corresponding contribution to the line shape function. Of course, there is no way that the set of calculated energy differences can match the set of frequencies selected in advance because the set of distances was chosen independently at the outset, and these are not the roots associated with the latter. A new problem thus arises because the calculated contributions to the line shape have to be added up; one cannot simply add them up as in the previous method. In fact, every set of calculated energy differences (i.e., the frequency detunings of the line shape) associated with different initial and final orientations are different from each other. This implies that the locations in the line shape function at which every set of calculated contributions are made are not fixed. However, with a spline interpolation, one is able to find the contributions corresponding to a fixed frequency set based on every set of calculated energy differences and calculated contributions. Therefore, without solving an equation in order to find its roots, one is still able to obtain a set of contributions corresponding to the set of frequencies selected in advance. Then, one can simply add the results obtained to get the line shape function. The difficulty of finding roots is no longer a problem, and one can, using this new method, introduce a more realistic anisotropic potential into consideration.

Based on this new method, in addition to the long-range dipole - dipole and dipole - quadrupole interactions considered previously for H_2O - H_2O and H_2O - N_2, respectively, we are able to add the short-range repulsive interaction represented by a site-site model. It turns out that the effects of short-range interaction to the far-wing line shape are important, and can change the shape appreciably. Thus, by adjusting the free potential parameters in this model, we can achieve substantially improved results that compare very well with Burch's measurements of the self- and foreigner-broadened continuum absorption coefficients at room temperature (see Figs. 1 and 2). Then, using this improved potential, we have repeated our previous calculations for other temperatures ranging from 220 K to 330 K and for frequencies from 400 cm^{-1} to 1600 cm^{-1}. These data have been tabulated for convenient use by other researchers, and can easily be extended in both temperature and frequency so as to obtain accurate theoretical continua for use as input in other programs. This last step will allow us to gauge the accuracy of the results by comparison with actual field measurements.

Publications

In addition to the journal articles and conference proceedings listed below, we are in the process of completing a manuscript summarizing the progress mentioned above, including new line shape functions and absorption coefficients for H_2O - H_2O and H_2O -N_2 for a range of temperatures. Some figures presented in this manuscript are reported here.

Journal Articles:

1. Ma, Q., R. H. Tipping, G. Birnbaum, and C. Boulet, The sum rules and the summery of the memory functions. *J. Quant. Spec. Radiat. Transfer*, **59**, 259-271, 1998.

2. Ma, Q., and R. H. Tipping, A far-wing line shape theory which satisfies the detailed balance principle. *J. Quant. Spec. Radiat. Transfer*, **59**, 245-257, 1998.

3. Ma, Q., and R. H. Tipping, The distribution of density matrices over potential-energy surfaces: Application of the calculation of the far-wing line shapes for CO_2. *J. Chem. Phys.*, **108**, 3386-3399, 1998.

4. Ma, Q., R. H. Tipping, C. Boulet, and J.-P. Bouanich, Theoretical far-wing line shape and absorption for high temperature CO_2. *Applied Optics*, 1999 (in press).

5. Moreau, G., J. Boissoles, C. Boulet, R. H. Tipping, and Q. Ma, Theoretical study of the collision-induced fundamental absorption spectra of O_2-O_2 pairs for temperatures between 193 K and 273 K. *J. Quant. Spec. Radiat. Transfer*, 1999 (in press).

Other Contributions:

1. Ma, Q., and R.H. Tipping, New formulation for far-wing line shapes: Application to CO_2 and H_2O. *The XIVth International Conference on Spectral Line Shapes*, June 22 - 26, 1998, Penn. State University.

<center>FIGURE CAPTIONS</center>

Fig. 1 (A). The self–broadened far–wing line shape of H_2O (in units of cm^{-1} atm^{-1}) as a function of frequency ω (in units of cm^{-1}) for T = 296 K.

Fig. 1 (B). The calculated self–broadened absorption coefficient (in units of cm^{-1} amagat^{-2}) at T = 296 K in the 300 − 1100 cm^{-1} spectral region is represented by Δ. For comparison, the experimental values are denoted by +.

Fig. 2 (A). The N_2–broadened far–wing line shape of H_2O (in units of cm^{-1} atm^{-1}) as a function of frequency ω (in units of cm^{-1}) for T = 296 K.

Fig. 2 (B). The calculated N_2–broadened absorption coefficient (in units of cm^{-1} amagat^{-2}) at T = 296 K in the 300 − 1100 cm^{-1} spectral region is represented by Δ. For comparison, the experimental values are denoted by +.
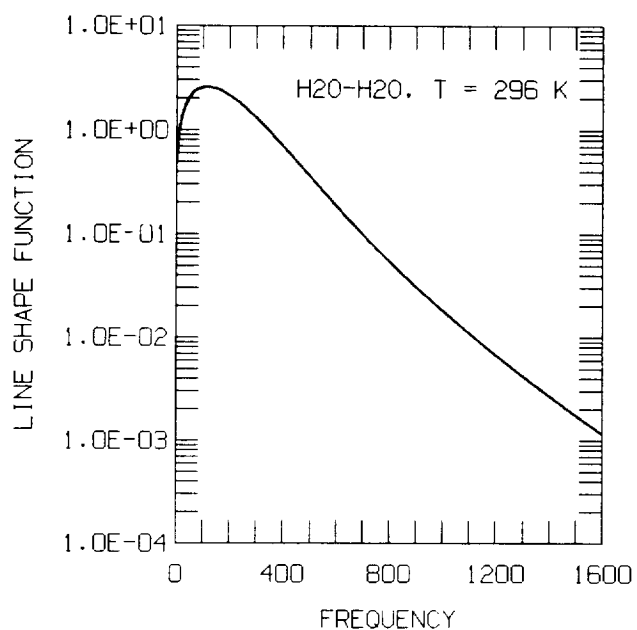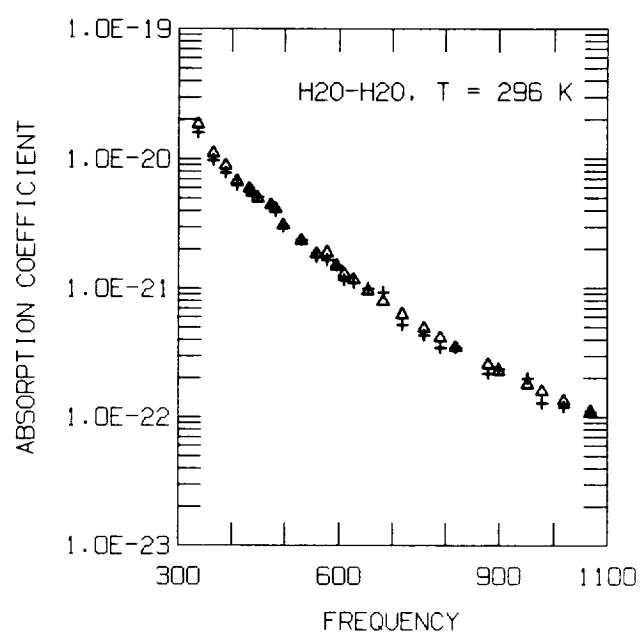
FIG. 1 (A)

FIG. 1 (B)

FIG. 2 (A)
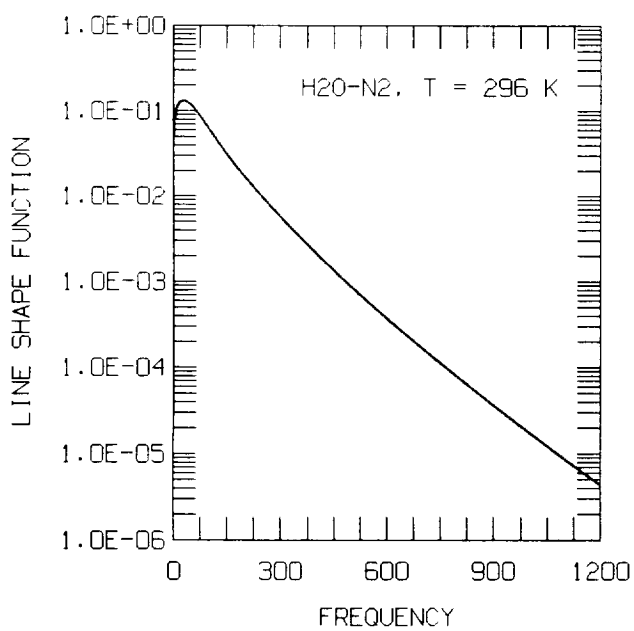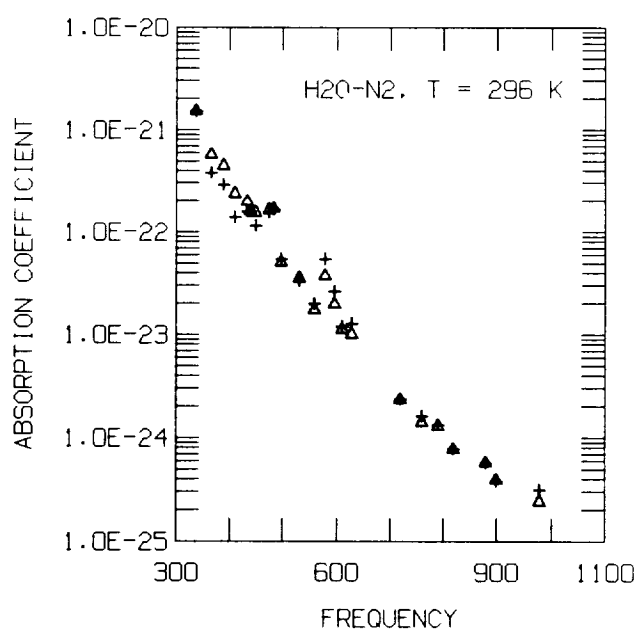
FIG. 2 (B)